Cambridge Pre-U

Cambridge International Examinations
Cambridge Pre-U Certificate

CHEMISTRY **9791/03**

Paper 3 Part B Written **May/June 2016**

MARK SCHEME

Maximum Mark: 100

Published

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Mark schemes should be read in conjunction with the question paper and the Principal Examiner Report for Teachers.

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This syllabus is approved for use in England, Wales and Northern Ireland as a Cambridge International Level 3 Pre-U Certificate.

This document consists of **10** printed pages.

Mark schemes will use these abbreviations:

;	separates marking points
/	alternatives
ORA	or reverse argument
ALLOW	for a non-ideal but allowable alternative valid point
NOT	answer is not credited
<u>underline</u>	actual word underlined must be used by candidate (grammatical variants excepted)
(xxx)	wording in brackets is for the clarity of the mark scheme but is not required
max	indicates the maximum number of marks that can be given
+	or **AND** statements on both sides of the **+** or **AND** are needed for that mark
ECF	error carried forward
IGNORE	for an answer that is not creditworthy but does not invalidate any additional creditworthy response

Question	Answer	Mark
1(a)(i)	Any **three** from the following: Gas molecules behave as rigid spheres (1) No intermolecular forces (1) Collisions are perfectly elastic (1) Molecules have no / negligible volume (1)	**3**
1(a)(ii)	Pressure of a gas (at constant temperature) is inversely proportional to volume (1)	**1**
1(a)(iii)	Volume of a gas (at constant pressure) is proportional to temperature (1)	**1**
1(a)(iv)	Low temperature and high pressure (1) Kinetic energy of the molecules decreases at low temperature so the intermolecular forces are more significant (1) At high pressure the volume of the molecules becomes increasingly significant (1)	**3**
1(a)(v)	H_2 > CH_4 > Cl_2 > CH_3Cl (1) CH_3Cl has permanent dipole (– permanent dipole) attraction **AND** H_2 / CH_4 / Cl_2 have instantaneous (dipole) – induced dipole attractions (1) Strength of instantaneous dipole – induced dipole is Cl_2 > CH_4 > H_2 linked to increased **number of electrons** (1) Permanent dipole(– permanent dipole) attraction greater than instantaneous dipole – induced dipole attractions (1)	**4**
1(b)(i)	Vertical axis = number of molecules (1) Horizontal = energy (1)	**2**
1(b)(ii)	Second curve has peak higher and to left of original peak (1) Finishes below original and does not touch *x*-axis (1)	**2**

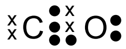
Question	Answer	Mark
1(b)(iii)	Activation energy shown on curve **AND** Reference to greater area beyond E_a at higher T / area under the curve is proportional to the number of molecules (1) Greater rate at higher temperature because more molecules collide with an energy greater than the activation energy (1)	**2**
1(c)(i)	(Using Expt 1 and 2) when [NO] doubles (and [O_2] stays the same) then the rate $\times$4, therefore order = 2 (1) (Using Expt 1 and 3) when [O_2] doubles (and [NO] stays the same) then the rate doubles, therefore order = 1 (1) Rate = $k[NO]^2[O_2]$ (1)	**3**
1(c)(ii)	$k = \text{rate} / [NO]^2[O_2] = 1.15 \times 10^{-14}/(1.25 \times 10^{-3})^2(1.25 \times 10^{-3})$ $= 5.89 \times 10^{-6}$ (1) units = $dm^6\,mol^{-2}\,s^{-1}$ (1)	**2**
1(c)(iii)	$p = nRT / V = 2.5 \times 10^{-3} \times 8.31 \times 80 / 1.0 \times 10^{-3}$ (1) $= 1.66 \times 10^3$ (Pa) (1)	**2**

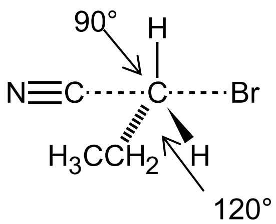
Question	Answer	Mark
2(a)(i)	Forward and reverse rates are equal (1)	**1**
2(a)(ii)	If the conditions of an equilibrium are changed equilibrium moves to reduce/oppose the change (1)	**1**
2(b)(i)	$\dfrac{[CO(g)]\,[H_2O(g)]}{[CO_2(g)]\,[H_2(g)]}$ (1)	**1**
2(b)(ii)	The forward reaction is endothermic as K_c increases as the temperature increases (1)	**1**
2(b)(iii)	There is no change (in equilibrium position) (1) There are equal number of moles (of gas) on each side (1)	**2**

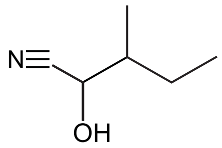
Question	Answer	Mark
2(b)(iv)	At equilibrium: moles of CO = 6.93×10^{-3} mol (1) moles of H_2 = $0.02 - 6.93 \times 10^{-3} = 3.07 \times 10^{-3}$ mol **AND** moles of CO_2 = $0.01 - 6.93 \times 10^{-3} = 1.307 \times 10^{-2}$ mol (1) $K_c = \dfrac{(6.93 \times 10^{-3} / V)^2}{(3.07 \times 10^{-3} / V)(1.307 \times 10^{-2} / V)} = 1.20$ (1)	3
2(c)(i)	$31.40 \times 0.2/1\,000 = 6.28 \times 10^{-3}$ = mol OH^- to neutralise 10 cm^3 (1) So OH^- to neutralise 1 dm^3 = $6.28 \times 10^{-3} \times 1000/10 = 0.628$ mol (1)	2
2(c)(ii)	At equilibrium: Moles of PCl_3 = moles of Cl_2 = x so moles of PCl_5 = $0.1 - x$ (1) Hence $5(0.1 - x) + 2(0.1 - x) + 3x + 2x = 0.628$ (1) $x = 0.036$, amount of PCl_5 = 0.064 mol (1)	3

Question	Answer	Mark
3(a)(i)	(Every atom has) 12 nearest neighbours (1)	1
3(a)(ii)	• 2 x * indicate 3rd layer in ABC i.e. octahedral holes (1) • ‘T’ shows a tetrahedral hole i.e. over atom in bottom or 2nd layer (1) • ‘O’ shows an octahedral hole i.e. between 1st and 2nd layer atoms (1)	3
3(a)(iii)	F^- ions occupy tetrahedral holes in the (CCP) lattice of Ca^{2+} (1) Ratio of tetrahedral holes to Ca^{2+} ions = 2:1 so F^- occupy **all** the tetrahedral holes (1)	2

Question	Answer	Mark
3(b)(i)	RFM of $SnCl_4$ = 260.7 **AND** RFM of $SnCl_2$ = 189.7 (1) % by mass of Sn in $SnCl_2$ = 62.6% **AND** % by mass of Sn in $SnCl_4$ = 45.5% (1) 62.6x / 100 + 45.5(100 – *x*) / 100 = 50 *x* = 25.9% (1)	**3**
3(b)(ii)	$E^{\ominus}$ (H^+ / H_2)is more positive than $E^{\ominus}$ (Sn^{2+} / Sn) but less positive than for $E^{\ominus}$ (Sn^{4+} / Sn^{2+}) so H^+ can oxidise Sn to Sn^{2+} (but not Sn^{2+} to Sn^{4+}) (1) $E^{\ominus}$ (Cl_2 / Cl^-)more positive than sum of $E^{\ominus}$ (Sn^{2+} / Sn) and $E^{\ominus}$ (Sn^{4+} / Sn^{2+}) so can also oxidise Sn^{2+} to Sn^{4+} (1) Predictions using $E^{\ominus}$ are limited to aqueous solutions and standard conditions (1)	**3**

Question	Answer	Mark
3(c)(i)	 (1)	1
3(c)(ii)	Covalent to ionic (down the group) (1) (C to Pb) electronegativity decreases / electronegativity difference increases (1)	2

Question	Answer	Mark
4(a)(i)	**M1**: curly arrow shown correctly (1) **M2**: lone pair on carbon of CN^- (1) **M3**: correct dipole on C–Br (1)  **M4**: trigonal bipyramid shown (1) **M5**: both bond angles correct (1)	5
4(a)(ii)	First step of mechanism with correct curly arrow (1) $(CH_3)_3C^+$ and Br^- shown (1) Tertiary carbocation is stabilised by (electron-release from) three methyl groups (1)	3
4(b)(i)	$C_3H_7CN + H_2O \rightarrow C_3H_7CONH_2$ (1)	1

Question	Answer	Mark
4(b)(ii)	($C_3H_7CONH_2 + H_2O + H^+$) → $C_3H_7COOH + NH_4^+$ (1)	**1**
4(b)(iii)	Hydrolysis (1) No change in FGL (1)	**2**
4(c)	$C_3H_7CH_2NH_2$ / 1-butanamine / 1-aminobutane / *n*-butylamine (1) Reduction (1) FGL falls (from carboxylic acid level to alcohol level) (1)	**3**
4(d)(i)	Nucleophilic addition (1)	**1**
4(d)(ii)	**W** =  (1)	**1**
4(d)(iii)	Nucleophilic substitution (1)	**1**
4(d)(iv)	PBr_3 / P + Br_2 (1)	**1**
4(d)(v)	NH_3 (1) In ethanol and warmed **OR** heat in sealed tube (1)	**2**
4(d)(vi)	$CH_3CH_2CH(CH_3)CH(NH_2)CN$ (1)	**1**
4(d)(vii)	Enantiomers: **D** / **A** (S-S / R-R) and **B** / **C** (S-R / R-S) (1) Diastereoisomers: **D** / **B** (S-S / S-R); **D** / **C** (S-S / R-S); **A** / **C** (R-R / R-S) and **A** / **B** (R-R / S-R) Award 2 marks for all 4 pairs Award 1 mark for 2 pairs	**3**

Question	Answer	Mark
5(a)(i)	C_4H_{10} (1)	**1**
5(a)(ii)	Isomer 1=$CH_3CH_2CH_2CH_3$ **AND** isomer 2 = $(CH_3)_3CH$ (1) Isomer 1: quartet due to CH_2 protons split by adjacent CH_3 **AND** triplet due to CH_3 protons split by CH_2 (1) Isomer 2: doublet due to CH_3 protons split by adjacent CH **AND** dectet due to CH proton split by 3 adjacent CH_3 groups (1)	**3**
5(b)(i)	Contain ^{79}Br and ^{81}Br (1) Equal abundance of molecular ions as isotopes exist in 50:50 ratio (1)	**2**
5(b)(ii)	C_3H_7Br (1)	**1**
5(b)(iii)	Isomer 3 = $(CH_3)_2CHBr$ **AND** isomer 4 = $CH_3CH_2CH_2Br$ (1) m/z 29 arises from a C_2H_5 fragment (1) m/z 109 and 107 due to loss of CH_3 or arises from CH_3CHBr or CH_2CH_2Br (1)	**3**
5(b)(iv)	$[C_3H_7Br]^+ \rightarrow [C_3H_7]^+ + Br$ **M1** = C_3H_7 as a product (1) **M2** = rest of equation (1)	**2**
5(c)(i)	Isomer 5 = $CH_3(CH_2)_3CHO$ giving alcohol $CH_3(CH_2)_3CH(C_2H_5)OH$ (1) Isomer 6 = $CH_3(CH_2)_2COCH_3$ giving $CH_3(CH_2)_2C(CH_3)(C_2H_5)OH$ (1) Isomer 7 = $(C_2H_5)_2CO$ giving $(C_2H_5)_3COH$ (1)	**3**
5(c)(ii)	$HCHO + C_2H_5MgBr + H_2O \rightarrow CH_3(CH_2)_2OH + Mg(OH)Br$ **M1** = $CH_3(CH_2)_2OH$ (1) **M2** = rest of equation (1)	**2**

Question	Answer	Mark
5(d)(i)	Isomer 8 and isomer 9 may be 2-methylphenol or 3-methylphenol (1) Isomer 10 is 4-methylphenol (1) Isomer 11 is phenylmethanol (1)	**3**
5(d)(ii)	(4) peaks in 125–150 ppm and (1) peak in 50–65 ppm (1)	**1**